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Chiral *versus* racemic building blocks in supramolecular chemistry: malate salts of organic diamines

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(*S*)-Malic acid forms a salt with *N*,*N*′-dimethylpiperazine, $[MeN(CH_2CH_2)_2NMe]H_2^{2+}\cdot 2C_4H_5O_5^-$ (1) (triclinic, $P1$, $Z' = 1$), in which the cations link pairs of hydrogen-bonded anion chains to form a molecular ladder. With 4,4′-bipyridyl, (*S*)-malic acid forms a 1:1 adduct which crystallizes from methanol to yield two polymorphs, (2) (triclinic, $P1$, $Z' = 1$) and (3) (monoclinic, $C2$, $Z' = 1$), while racemic malic acid with 4,4′-bipyridyl also forms a 1:1 adduct, (4) (monoclinic, $P2_1/c$, $Z' = 1$). In each of (2), (3) and (4) the components are linked by O—H···N and N—H···O into chains of alternating bipyridyl and malate units, which are linked into sheets by O—H···O hydrogen bonds. In each of the 1:1 adducts (5) and (6), formed by, respectively, (*S*)-malic acid and racemic malic acid with 1,2-bis(4′-pyridyl)ethene, the diamine is disordered over two sets of sites, related by a 180° rotation about the N···N vector. In (5), $(C_{12}H_{10}N_2)H^+\cdot C_4H_5O_5^-$ (triclinic, $P1$, $Z' = 1$), the components are again linked by a combination of N—H···O and O—H···O hydrogen bonds into sheets, while in (6) (triclinic, $P\overline{1}$, $Z' = 0.5$) there is only partial transfer of the H atom from O to N and the malate component is disordered across a centre of inversion. With 1,4-diazabicyclo[2.2.2]octane, racemic malic acid forms a 1:2 salt, $[(C_6H_{12}N_2)H_2]^{2+}\cdot 2C_4H_5O_5^-$ (7) (monoclinic, $P2_1/c$, $Z' = 2$), while (*S*)-malic acid forms a 1:1 adduct, (8) (monoclinic, $P2_1$, $Z' = 3$). There are thus six independent molecular components in each. In (7) the ions are linked by an extensive series of N—H···O and O—H···O hydrogen bonds into a three-dimensional framework, but in (8) there is extensive disorder involving all six components, and no refinement proved to be feasible.

1. Introduction

In hydrogen-bonded adducts of simple bisphenols or dicarboxylic acids with tertiary diamines, the primary mode of supramolecular aggregation is chain formation by hard (Braga *et al.*, 1995) O—H···N and/or N—H···O hydrogen bonds (Coupar *et al.*, 1997; Ferguson *et al.*, 1997, 1998; Glidewell *et al.*, 1999; Lavender *et al.*, 1999). The mutual disposition of the hydrogen-bonded chains is often determined by soft (Braga *et al.*, 1995) hydrogen bonds, usually of the C—H···O type, or by aromatic $\pi\cdots\pi$ stacking interactions.

Where both components in such a system are achiral, the adducts generally crystallize in centrosymmetric space groups, as the occurrence of inversion centres, especially unoccupied inversion centres, seems to be particularly favourable in molecular crystals (Brock & Dunitz, 1994). Similar consid-

Table 1
Experimental details.

	(1)	(2)	(3)	(4)	(5)
Crystal data					
Chemical formula	$C_6H_{16}N_2\cdot 2C_4H_5O_5$	$C_{10}H_{8.5}N_2\cdot C_4H_{5.5}O_5$	$2C_{10}H_{8.5}N_2\cdot 2C_4H_{5.5}O_5$	$C_{10}H_{8.5}N_2\cdot C_4H_{5.5}O_5$	$C_{12}H_{11}N_2\cdot C_4H_5O_5$
Chemical formula weight	382.37	290.27	580.54	290.27	316.31
Cell setting, space group	Triclinic, $P1$	Triclinic, $P1$	Monoclinic, $C2$	Monoclinic, $P2_1/c$	Triclinic, $P1$
a, b, c (Å)	5.8757 (3), 7.8751 (4), 10.6165 (7)	5.1647 (4), 6.2749 (5), 10.2126 (9)	20.500 (4), 4.6656 (9), 14.201 (3)	14.1274 (8), 4.7459 (3), 20.1749 (13)	4.9325 (3), 8.3343 (4), 9.3502 (7)
α, β, γ (°)	70.345 (2), 74.500 (2), 87.435 (3)	83.235 (3), 89.808 (3), 79.601 (3)	90, 99.68 (3), 90	90, 100.565 (3), 90	72.751 (2), 89.414 (2), 80.207 (2)
V (Å^3)	445.24 (4)	323.21 (5)	1338.9 (5)	1329.74 (14)	361.41 (4)
Z	1	1	2	4	1
D_x (Mg m^{-3})	1.426	1.491	1.440	1.450	1.453
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	1913	1351	1263	3105	1174
θ range (°)	2.75–27.55	3.67–27.43	2.68–25.04	2.73–27.51	4.20–25.15
μ (mm^{-1})	0.122	0.115	0.111	0.112	0.109
Temperature (K)	293 (2)	150 (2)	150 (2)	150 (2)	150 (2)
Crystal form, colour	Plate, colourless	Block, colourless	Needle, colourless	Needle, colourless	Plate, colourless
Crystal size (mm)	0.35 × 0.27 × 0.13	0.40 × 0.30 × 0.30	0.25 × 0.12 × 0.12	0.28 × 0.12 × 0.12	0.32 × 0.30 × 0.18
Data collection					
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.9587	0.9555	0.9728	0.9694	0.9658
T_{max}	0.9844	0.9663	0.9868	0.9867	0.9806
No. of measured, independent and observed parameters	6309, 2041, 1476	3702, 1465, 1195	4367, 1343, 963	11 155, 3029, 1416	3171, 2167, 1958
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.065	0.036	0.070	0.0114	0.051
θ_{max} (°)	27.55	27.43	25.04	27.51	25.15
Range of h, k, l	$0 \rightarrow h \rightarrow 7$ $-10 \rightarrow k \rightarrow 10$ $-12 \rightarrow l \rightarrow 13$	$0 \rightarrow h \rightarrow 6$ $-7 \rightarrow k \rightarrow 8$ $-13 \rightarrow l \rightarrow 13$	$-23 \rightarrow h \rightarrow 24$ $-5 \rightarrow k \rightarrow 4$ $-16 \rightarrow l \rightarrow 16$	$0 \rightarrow h \rightarrow 18$ $0 \rightarrow k \rightarrow 6$ $-26 \rightarrow l \rightarrow 25$	$-5 \rightarrow h \rightarrow 5$ $-9 \rightarrow k \rightarrow 9$ $-11 \rightarrow l \rightarrow 11$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.1109, 0.978	0.0478, 0.1303, 1.032	0.0452, 0.1226, 1.052	0.0604, 0.1892, 0.972	0.0549, 0.1427, 1.095
No. of reflections and parameters used in refinement	2041, 242	1465, 195	1343, 194	3029, 194	2167, 179
H-atom treatment	Constrained	Constrained	Constrained	Constrained	Constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0823P)^2 + 0.0245P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.1485P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0815P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.1P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000	0.000	0.000	0.000	0.004
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.186, −0.152	0.412, −0.245	0.209, −0.202	0.266, −0.291	0.311, −0.274
Extinction method	*SHELXL*	None	*SHELXL*	*SHELXL*	None
Extinction coefficient	0.106 (18)	–	0.009 (3)	0.008 (2)	–

	(6)	(7)
Crystal data		
Chemical formula	$2C_6H_5N\cdot C_4H_6O_5$	$C_6H_{14}N_2\cdot 2C_4H_5O_5$
Chemical formula weight	316.31	380.35
Cell setting, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a, b, c (Å)	4.9566 (6), 8.4178 (10), 9.2538 (14)	12.7309 (3), 20.9103 (5), 12.5400 (3)
α, β, γ (°)	73.213 (5), 89.915 (6), 79.750 (7)	90, 95.1780 (13), 90
V (Å^3)	363.24 (8)	3324.61 (14)
Z	1	8
D_x (Mg m^{-3})	1.446	1.520
Radiation type	Mo $K\alpha$	Mo $K\alpha$

Table 1 (continued)

	(6)	(7)
No. of reflections for cell parameters	1243	7524
θ range (°)	2.91–25.14	2.58–27.48
μ (mm^{-1})	0.109	0.130
Temperature (K)	150 (2)	150 (2)
Crystal form, colour	Plate, colourless	Block, colourless
Crystal size (mm)	0.30 × 0.30 × 0.12	0.32 × 0.28 × 0.25
Data collection		
Diffractometer	Nonius KappaCCD	Nonius KappaCCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan
T_{min}	0.9681	0.9596
T_{max}	0.9870	0.9682
No. of measured, independent and observed parameters	3458, 1286, 774	27 049, 7603, 4395
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.078	0.070
θ_{max} (°)	25.14	27.48
Range of h, k, l	$-5 \rightarrow h \rightarrow 0$ $-10 \rightarrow k \rightarrow 9$ $-10 \rightarrow l \rightarrow 11$	$-16 \rightarrow h \rightarrow 16$ $-27 \rightarrow k \rightarrow 0$ $0 \rightarrow l \rightarrow 16$
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0593, 0.1785, 1.024	0.0551, 0.1676, 1.025
No. of reflections and parameters used in refinement	1286, 131	7603, 477
H-atom treatment	Constrained	Constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0867P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0827P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000	0.000
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.226, −0.238	0.357, −0.405
Extinction method	None	None

Computer programs used: *Kappa-CCD* (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS*97 (Sheldrick, 1997*a*), *SHELXL*97 (Sheldrick, 1997*b*), *PLATON* (Spek, 2001), *PRPKAPPA* (Ferguson, 1999).

erations apply if one component of such a system is a racemic mixture of the two enantiomers of a chiral building block (Burchell *et al.*, 2000, 2001). However, if one or other component is a single enantiomer of a chiral acid or amine, then this places major constraints on the range of accessible space groups. Overall, there is a very high likelihood that the use of a single enantiomeric form of one component will lead to a different space group, and hence a different supramolecular arrangement, from that found with a racemic component.

Although malic acid (2-hydroxy-1,4-butanedioic acid, $C_4H_6O_5$) is one of the simplest chiral dicarboxylic acids, there have been rather few studies of its role in supramolecular chemistry. Studies of the salts formed with primary amines and diamines (Aakeröy & Nieuwenhuyzen, 1994, 1996) utilized only (*S*)-malic acid, and were primarily concerned with the two-dimensional arrays formed by the anions $C_4H_5O_5^-$ and $C_4H_4O_5^{2-}$. A single report involving racemic malic acid concerned the salt of an unusual diamine containing both primary and secondary N centres, which was obtained adventitiously as a by-product in the synthesis of copper(II) coordination polymers (Kansikas, 1985). In this context, it may be noted here that, whereas pure (*S*)-malic acid crystallizes in space group $P2_1$ (van der Sluis & Kroon, 1989), the corresponding racemic acid forms two polymorphs, denoted as the α and β forms, which crystallize in space groups *Cc* (van Loock *et al.*, 1981) and $P2_1/c$ (van der Sluis & Kroon, 1985), respectively.

In the present study, the rationale informing the use of bis-tertiary or bis-heteroaromatic amines is the attempt to constrain the acid–base interactions to chain-formation only, in order to render the resulting supramolecular structures as simple as possible, the better to assess the effect of using chiral *versus* racemic building blocks, in such cases as corresponding pairs of salts can be prepared in suitable crystalline form. Here, we report the synthesis and structures of the salt-type adducts formed between malic acids (chiral or racemic) and *N*,*N*′-dimethylpiperazine [MeN(CH$_2$CH$_2$)$_2$NMe], giving (1), 4,4′-bipyridyl ($NC_5H_4C_5H_4N$), (2)–(4), 1,2-bis-(4′-pyridyl)-ethene ($NC_5H_4CH{=}CHC_5H_4N$), (5) and (6), and 1,4-diazabicyclo[2.2.2]octane [DABCO; N(CH$_2$CH$_2$)$_3$N], (7) and (8).

2. Experimental

2.1. Synthesis

Equimolar quantities of the appropriate malic acid [(*S*) or racemic] and the appropriate amine were separately dissolved in methanol: the solutions were mixed and set aside to crystallize, giving analytically pure samples of (1)–(8). The two

Table 2
Hydrogen-bond parameters (Å, °).

D—H···A	H···A	D···A	D—H···A
(1)			
N1—H1···O21	1.90	2.736 (4)	151†
N1—H1···O25	2.16	2.824 (4)	129†
N4—H4···O11	1.87	2.710 (4)	152‡
N4—H4···O15	2.21	2.849 (4)	126‡
O13—H13···O12	1.67	2.480 (4)	169
O23—H23···O22	1.69	2.494 (4)	167
O15—H15···O12^{i}	1.95	2.763 (4)	172
O25—H25···O22^{ii}	1.93	2.751 (3)	173
C6—H6*A*···O23^{iii}	2.54	3.476 (5)	163
C7—H7*A*···O24^{iii}	2.57	3.453 (6)	153
C7—H7*C*···O13^{iv}	2.55	3.489 (6)	167
C8—H8*A*···O14^{v}	2.52	3.408 (5)	153
(2)			
N11—H11···O1	1.67	2.553 (4)	175
O1—H1···N11	1.71	2.553 (4)	175
O3—H3···N21^{vi}	1.75	2.588 (4)	176
O5—H5···O1	2.16	2.646 (3)	117§
O5—H5···O3^{vii}	2.20	2.823 (4)	131§
C13—H13···O4^{viii}	2.35	3.280 (5)	167
C15—H15···O2^{ix}	2.56	3.477 (4)	163
C23—H23···O2^{ix}	2.38	3.324 (4)	170
C25—H25···O4^{viii}	2.47	3.420 (5)	176
(3)			
N21—H21···O3^{x}	1.75	2.627 (5)	179
O3—H3···N21^{xi}	1.79	2.627 (5)	173
O1—H1···N11	1.71	2.541 (5)	169
O5—H5···O2	2.33	2.702 (4)	107¶
O5—H5···O2^{xii}	2.12	2.932 (4)	162¶
C15—H15···O4^{xiii}	2.48	3.403 (5)	165
C16—H16···O1^{xiv}	2.46	3.407 (6)	173
(4)			
N11—H11···O1	1.67	2.549 (3)	176
O1—H1···N11	1.74	2.549 (3)	161
O3—H3···N21^{xv}	1.81	2.638 (4)	171
O5—H5···O2	2.31	2.716 (3)	110††
O5—H5···O2^{xvi}	2.08	2.889 (3)	161††
C12—H12···O2^{xvii}	2.44	3.360 (4)	164
C13—H13···O5^{xviii}	2.48	3.302 (4)	145
C16—H16···O1^{xix}	2.39	3.327 (4)	169
C23—H23···O4^{xix}	2.49	3.434 (4)	170
(5)			
N11—H11···O2	1.44[a]	2.561 (3)	171
O4—H4···N21^{xx}	1.76	2.591 (3)	172
O5—H5···O1^{i}	1.86	2.702 (3)	175
C16—H16···O4^{xxi}	2.51	3.451 (7)	171
C23—H23···O1^{xxii}	2.52	3.136 (5)	123
C26—H26···O2^{xxiii}	2.49	3.401 (7)	160
C27—H27···O5^{xxii}	2.57	3.393 (6)	145
(6)			
O1—H1···N11	1.29[b]	2.556 (2)	168
O5—H5···O2^{i}	1.46[c]	2.606 (4)	173
C16—H16···O1^{xxiv}	2.31	3.231 (6)	162
C17—H17···O5^{xxii}	2.44	3.336 (6)	163
(7)			
N11—H11···O31	1.79	2.634 (2)	150
N12—H12···O51	1.74	2.610 (2)	154
N21—H21···O61	1.79	2.631 (2)	148
N22—H22···O41	1.77	2.629 (2)	153
O34—H34···O52^{xxv}	1.80	2.611 (2)	161
O35—H35···O62^{xxvi}	1.88	2.700 (2)	165
O44—H44···O42^{xxvii}	1.83	2.631 (2)	160
O45—H45···O32^{v}	1.90	2.709 (2)	161
O54—H54···O32^{xxviii}	1.83	2.649 (2)	166
O55—H55···O42^{xvi}	1.91	2.732 (2)	167
O64—H64···O62^{xxix}	1.80	2.630 (2)	167
O65—H65···O52	1.87	2.699 (2)	169
C12—H12*B*···O44^{xxx}	2.41	3.252 (3)	143
C15—H15*B*···O43^{xxxi}	2.34	3.258 (3)	154
C22—H22*A*···O54^{xxx}	2.45	3.390 (3)	158
C23—H23*B*···O32^{xxxii}	2.46	3.391 (3)	156
C26—H26*B*···O33^{xxxii}	2.28	3.265 (3)	171

Symmetry codes: (i) 1+ x, y, z; (ii) $x-1, y, z$; (iii) $x-1, y, 1+z$; (iv) $1+x, 1+y, z-1$; (v) $1+x, y, z-1$; (vi) $x-2, y-1, z-1$; (vii) $x, 1+y, z$; (viii) $1+x, y, 1+z$; (ix) $1+x, 1+y, z$; (x) $x, y-2, 1+z$; (xi) $x, 2+y, z-1$; (xii) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (xiii) $-x, y-1, 1-z$; (xiv) $-x, y, 1-z$; (xv) $x-1, y-2, z$; (xvi) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (xvii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (xviii) $1-x, \frac{3}{2}+y, \frac{1}{2}-z$; (xix) $1-x, 1-y, -z$; (xx) $3+x, y-1, z-1$; (xxi) $x-1, 1+y, z$; (xxii) $x-2, 1+y, z$; (xxiii) $x-2, y, 1+z$; (xxiv) $-x, 2-y, 1-z$; (xxv) $-x, -y, 1-z$; (xxvi) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (xxvii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (xxviii) $-x, -y, 2-z$; (xxix) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (xxx) $1-x, -y, 1-z$; (xxxi) $x-1, \frac{1}{2}-y, \frac{1}{2}+z$; (xxxii) $1+x, \frac{1}{2}-y, z-\frac{1}{2}$. Notes: (*a*) N11—H11 1.13 Å, (*b*) O1—H1 1.28 Å, (*c*) O5—H5 1.15 Å. † Three-centre N—H···$(O)_2$ system; sum of angles at H1 359°. ‡ Three-centre N—H···$(O)_2$ system; sum of angles at H4 357°. § Three-centre O—H···$(O)_2$ system; sum of angles at H5 359°. ¶ Three-centre O—H···$(O)_2$ system; sum of angles at H5 356°. †† Three-centre O—H···$(O)_2$ system; sum of angles at H5 360°.

polymorphs (2) and (3) crystallized from the same mixture and were separated by hand. Analyses: (1), found: C 44.1, H 7.2, N 7.3%; $C_{14}H_{26}N_2O_{10}$ requires: C 44.0, H 6.9, N 7.3%; (2), found: C 58.0, H 4.8, N 9.8%; $C_{14}H_{14}N_2O_5$ requires: C 57.9, H 4.9, N 9.7%; (3), found: C 58.0, H 4.8, N 9.8%; $C_{14}H_{14}N_2O_5$ requires: C 57.9, H 4.9, N 9.7%; (4), found: C 57.9, H 4.9, N 9.8%; $C_{14}H_{14}N_2O_5$ requires: C 57.9, H 4.9, N 9.7%; (5), found: C 60.8, H 5.3, N 9.0%; $C_{16}H_{16}N_2O_5$ requires: C 60.8, H 5.1, N 8.9%; (6), found: C 61.1, H 4.7, N 8.9%; $C_{16}H_{16}N_2O_5$ requires: C 60.8, H 5.1, N 8.9%; (7), found: C 44.4, H 6.9, N 7.4%; $C_{14}H_{24}N_2O_{10}$ requires: C 44.2, H 6.4, N 7.4%; (8), found: C 49.1, H 7.5, N 11.5%; $C_{10}H_{18}N_2O_5$ requires: C 48.8, H 7.4, N 11.4%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples. Although it was possible to synthesize reproducibly a 1:2 adduct of *N*,*N*′-dimethylpiperazine and racemic malic acid, analogous to (1), repeated attempts to produce crystals suitable for single-crystal X-ray diffraction have been consistently unsuccessful.

2.2. Data collection, structure solution and refinement

Diffraction data for (2)–(8) were collected at 150 (2) K [293 (2) K for (1)] using a Nonius KappaCCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Other details of cell data, data collection and refinement are summarized in Table 1, together with details of the software employed.

Compounds (1), (2), (5) and (6) are all triclinic. The space group $P\overline{1}$ was chosen for (6) and $P1$ for each of (1), (2) and (5), and in each case these were confirmed by analysis. For (3) the systematic absences permitted $C2$, Cm and $C2/m$ as possible space groups; $C2$ was chosen, and confirmed by the analysis. For (4) and (7) the space group $P2_1/c$ was uniquely assigned from the systematic absences. For (8) the systematic absences permitted $P2_1$ and $P2_1/m$ as possible space groups, and $P2_1$ was chosen on the grounds that the starting malic acid was chiral. The unit-cell dimensions for (8) [a = 11.3137 (5), b = 8.8394 (4), c = 17.6687 (9) Å; β = 97.9517 (17)°] indicated Z' =

3, and the structure could be solved to reveal six independent molecular components, all exhibiting serious disorder even at 150 K. Several data sets were collected using different crystals from different preparations, but with the same outcome on each occasion. No refinement of this structure proved to be feasible.

The structures were solved by direct methods and refined with all data on F^2. A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). For (1), (2), (3) and (5) the refined values of the Flack parameter (Flack, 1983) [−1.9 (6), 1.3 (17), 0 (3) and 1.4 (17), respectively] were inconclusive (Flack & Bernardinelli, 2000). Hence, for these compounds the Friedel equivalents were merged before the final refinements. In (5), where the diamine is disordered over two sets of sites, the coordinates of the N atoms in the two orientations were constrained to be identical, and all of the C and N atoms in both orientations were refined isotropically, when the site-occupation factors for the two orientations refined to 0.529 (4) and 0.471 (4), respectively. Similarly, in (6), where the two orientations of the diamine had equal occupancies, the coordinates of the N atoms for the two orientations were again constrained to be identical. In (6) the acid molecule is disordered about an inversion centre and the amine is also disordered about another inversion centre, but in this case anisotropic refinement was possible for the C and N atoms of the diamine. Atoms H1 and H5 bonded to atoms O1 and O5 were clearly visible in difference maps almost midway between the O and N atoms (involved in the O···H···N hydrogen bonds), and they were allowed for using the *SHELXL*97 *AFIX*148 command (Sheldrick, 1997*a*). All other H atoms were located from difference maps and included in the refinements as riding atoms, with O—H 0.82–0.84, N—H 0.88–0.93 and C—H 0.92–1.00 Å.

The diagrams were prepared with the aid of *PLATON* (Spek, 2001). Details of the hydrogen-bond dimensions are given in Table 2.[1] Figs. 1–25 show the molecular components, with the atom-labelling schemes and aspects of the supramolecular structures.

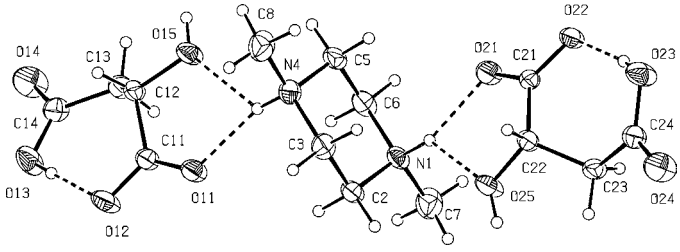

Figure 1
The molecular components of (1), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% probability level.

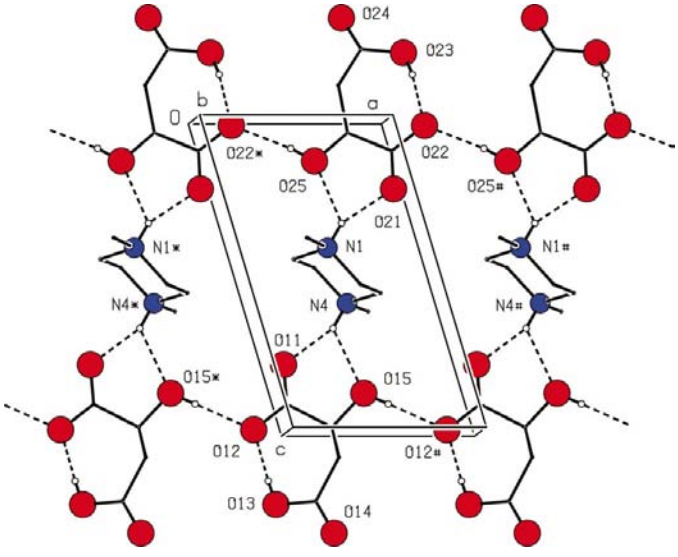

Figure 2
Part of the crystal structure of (1), showing the formation of a molecular ladder along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($x - 1, y, z$) and ($1 + x, y, z$), respectively.

3. Results and discussion

3.1. Hard hydrogen bonds generate one-dimensional arrays

3.1.1. *N*,*N*′-Dimethylpiperazine–(*S*)-malic acid (1/2), (1). The 1:2 adduct (1) formed between *N*,*N*′-dimethylpiperazine and (*S*)-malic acid is a salt, $[MeN(CH_2CH_2)_2NMe]H_2^{2+}\cdot 2C_4H_5O_5^-$, in which the H-atom transfer is from the carboxyl groups containing atoms C11 and C21, and in which all the H-atom sites are fully ordered (Fig. 1). In space group *P*1, all the ions are in general positions and the asymmetric unit can be placed arbitrarily within the unit cell. For the sake of convenience, the cation, in which the methyl groups occupy equatorial sites, has been centred at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The

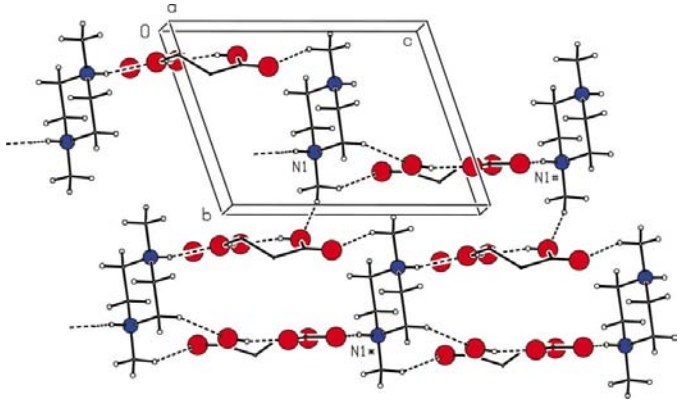

Figure 3
Part of the crystal structure of (1), showing the linking of the [100] ladders by the soft hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms in the anions have been omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($x, 1 + y, z$) and ($x - 1, y, 1 + z$), respectively.

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0134). Services for accessing these data are described at the back of the journal.

two independent anions each form, by means of O—H···O hydrogen bonds, a chain containing only one type of anion, and these chains are pairwise linked by the cations to form molecular ladders.

In the chain formed by the anions of type 1 (containing atom C11), hydroxyl atom O15 at (x, y, z) acts as a hydrogen-bond donor to carboxylate atom O12 at ($1 + x$, y, z), so producing, by translation, a $C(5)$ chain running parallel to [100]. The anions of type 2 (containing atom C21) form an antiparallel chain, in which atom O25 at (x, y, z) acts as a donor to atom O22 at ($x - 1$, y, z) (Fig. 2). The two chain types thus have opposite polarity but the same chirality. The type 1 chain lies in the domain $0.06 < y < 0.43$, while the type 2 chain occupies the domain $0.56 < y < 0.93$.

Each cation forms two essentially planar, but asymmetric, three-centre N—H···$(O)_2$ hydrogen bonds, both wholly within the asymmetric unit (Fig. 1). Atom N1 acts as a donor to atoms O21 and O25, and atom N4 as a donor to atoms O11 and O15. The hydrogen bonds to the anionic atoms O11 and O21 are significantly shorter than those to the neutral atoms O15 and O25. The net effect of the N—H···O hydrogen bonds is to link pairs of chains (Fig. 2). The resulting one-dimensional supramolecular structure is a molecular ladder, in which an antiparallel pair of $C(5)$ chains form the uprights and the cations form the rungs.

It is evident (Fig. 2) that the $P1$ structure of (1) closely mimics a centrosymmetric $P\overline{1}$ structure. This is particularly emphasized by the location of the cation at the centre of the $P1$ unit cell. The intramolecular hydrogen bonds in the two independent anions hold the anion configurations, so that the atomic coordinates of all atoms, apart from C13 and C23 and their associated H atoms, are close to a centrosymmetric array. The related salt formed by (*S*)-malic acid with piperazine itself is a monohydrate, crystallizing in space group $P2_12_12_1$, so that the mimicry of a centrosymmetric structure is not apparent in this case (Aakeröy & Nieuwenhuyzen, 1996). Indeed, it appears that where such salts crystallize as hydrates, such pseudosymmetry is generally absent (Aakeröy & Nieuwenhuyzen, 1994, 1996).

All the C—H bonds in the cation of (1) are adjacent to a cationic N. Hence, there are a number of C—H···O hydrogen bonds, albeit rather weak, formed by the cation as a donor, where the acceptors all lie in other ladders. Thus, atoms C6 and C7 in the cation at (x, y, z), which lies in the ladder along (x,$\frac{1}{2}$,$\frac{1}{2}$), act as donors, *via* atoms H6*A* and H7*A*, to atoms O23 and O24, respectively, both at ($x - 1$, y, $1 + z$), which are

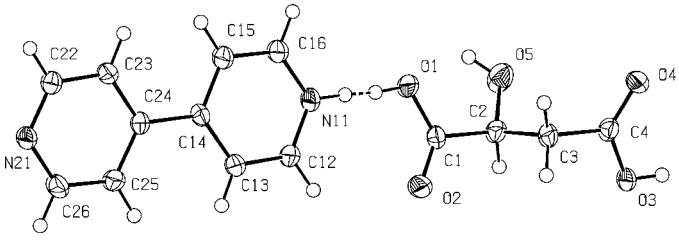

Figure 4
The molecular components of (2), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% probability level. The H atom between atoms O1 and N11 is disordered over two sites with equal occupancy.

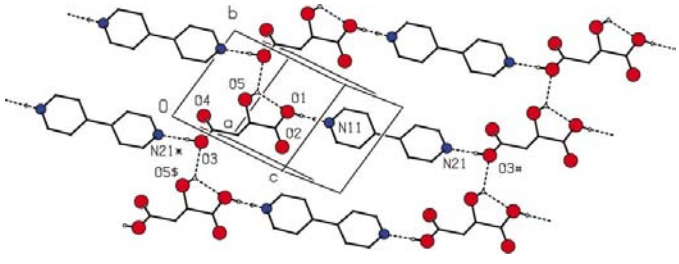

Figure 5
Part of the crystal structure of (2), showing the formation of a $(10\overline{2})$ sheet built from $R_6^6(38)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions ($x - 2$, $y - 1$, $z - 1$), ($2 + x$, $1 + y$, $1 + z$) and (x, $y - 1$, z), respectively.

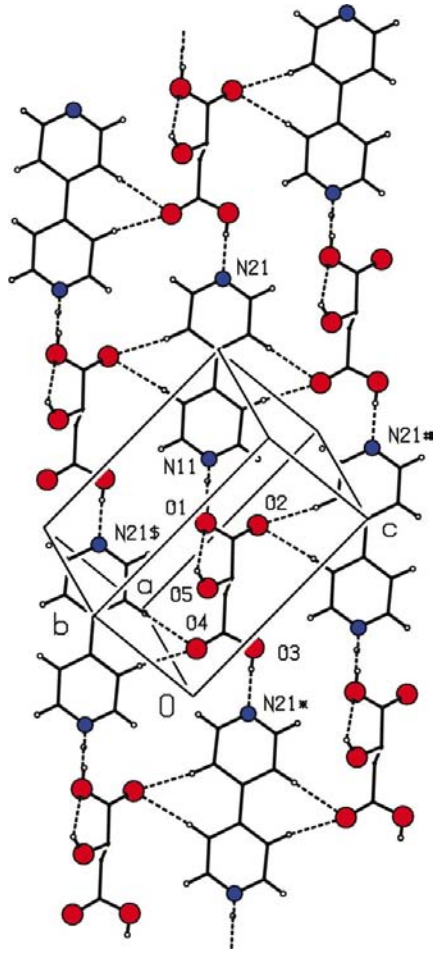

Figure 6
Part of the crystal structure of (2), showing the linking of the $(10\overline{2})$ sheets by the soft hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms in the anion have been omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions ($x - 2$, $y - 1$, $z - 1$), ($x - 1$, $y - 1$, z) and ($x - 1$, y, $z - 1$), respectively.

components of the ladder along $(x,\frac{1}{2},\frac{3}{2})$. Similarly, atom C7 at (x, y, z) acts as a donor, *via* atom H7*C*, to atom O13 at $(1 + x, 1 + y, z - 1)$, a component of the ladder along $(x,\frac{3}{2},-\frac{1}{2})$, and atom C8 at (x, y, z) acts as a donor, *via* atom H8*A*, to atom O14 at $(1 + x, y, z - 1)$ in the ladder along $(x,\frac{1}{2},-\frac{1}{2})$. In this manner, all the ladders are weakly linked into a continuous array (Fig. 3).

3.2. Hard hydrogen bonds generate two-dimensional arrays

Crystallization of (*S*)-malic acid with 4,4′-bipyridyl from methanol solutions yielded two polymorphs of a 1:1 adduct, a triclinic form (2) with space group *P*1, and a monoclinic form (3), with space group *C*2, whereas analogous treatment of the racemic malic acid yielded a single monoclinic form (4), with space group $P2_1/c$. Thus, the above conjecture concerning centrosymmetric and noncentrosymmetric space groups is valid for this system. It may be noted here that space groups *C*2 and $P2_1/c$ are isomorphic.

3.2.1. The triclinic polymorph (2) of 4,4′-bipyridyl–(*S*)-malic acid (1/1). In (2) the carboxyl group based on atom C1, adjacent to the hydroxyl group, participates in the disordered hydrogen bond between atoms O1 and N11 within the asymmetric unit (Fig. 4). With equal occupancies for the H sites, there are thus equal numbers of O—H···N and N—H···O hydrogen bonds at sites of this type. The carboxyl atom C4 at (x, y, z) forms a fully ordered O—H···N hydrogen bond with atom N21 at $(x - 2, y - 1, z - 1)$, so generating, by translation, a $C_2^2(16)$ chain running parallel to the [211] direction (Fig. 5). Just one such chain passes through each unit cell, and hence all the chains in the crystal have the same polarity and chirality. At the same time, the hydroxyl atom O5 at (x, y, z) acts as a hydrogen-bond donor to the neutral carboxyl atom O3 at $(x, 1 + y, z)$, so generating a second translational chain motif, a

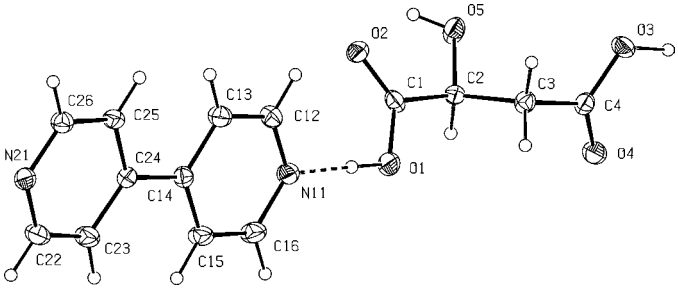

Figure 7
The molecular components of (3), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% probability level.

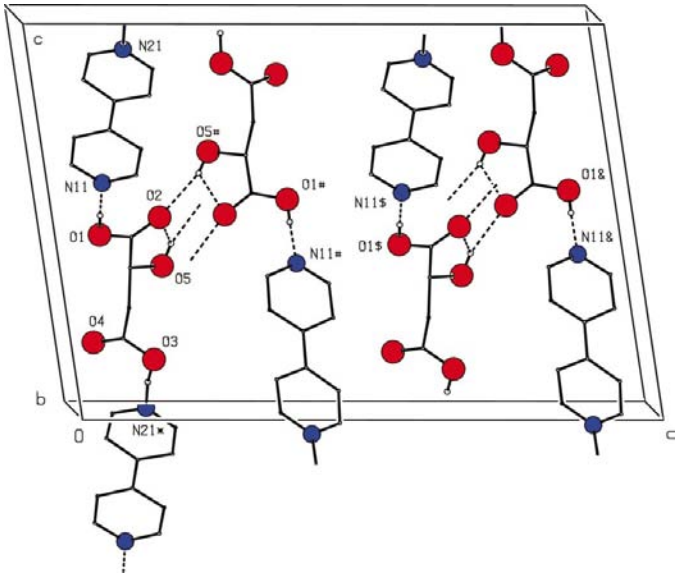

Figure 8
Part of the crystal structure of (3), showing the formation of the $[02\bar{1}]$ and [021] chains. For the sake of clarity, H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(x, 2 + y, z - 1)$, $(\frac{1}{2} - x, y - \frac{1}{2}, 1 - z)$, $(\frac{1}{2} + x, y - \frac{1}{2}, z)$ and $(1 - x, y, 1 - z)$, respectively.

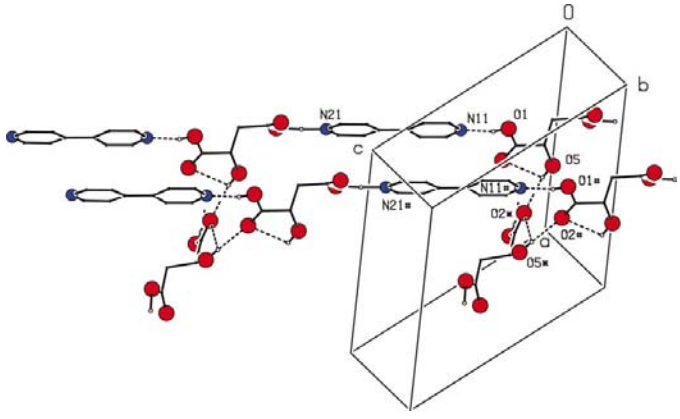

Figure 9
Part of the crystal structure of (3), showing the formation of (100) sheets by the linking of the $[02\bar{1}]$ chains. For the sake of clarity, H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(\frac{1}{2} - x, \frac{1}{2} + y, 1 - z)$ and $(x, 1 + y, z)$, respectively.

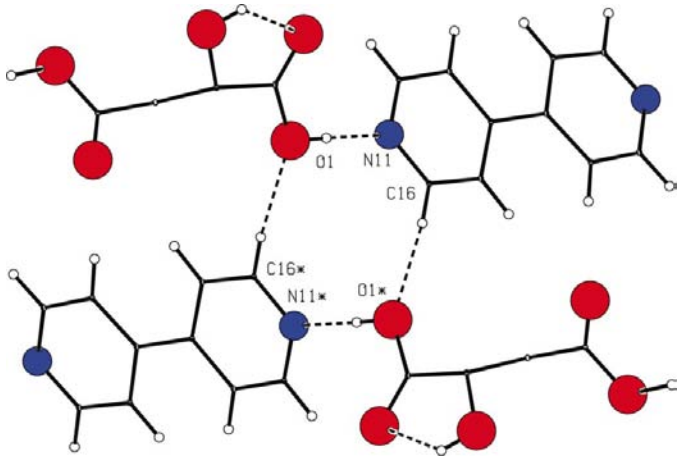

Figure 10
Part of the crystal structure of (3), showing the ring motif formed by soft hydrogen bonds which link the (100) sheets. For the sake of clarity, H atoms bonded to C atoms in the anion have been omitted. The atoms marked with an asterisk (*) are at the symmetry position $(-x, y, 1 - z)$.

$C(6)$ chain parallel to the [010] direction. The combination of these two chain motifs generates continuous sheets parallel to the $(10\bar{2})$ plane and built from a single type of $R_6^6(38)$ ring (Fig. 5).

The $(10\bar{2})$ sheets are linked both by a number of nearly linear C—H···O hydrogen bonds and by aromatic $\pi\cdots\pi$ stacking interactions, which involve both rings of the bipyridyl unit. Atoms C13 and C25 in the bipyridyl unit at (x, y, z) both act as donors to atom O4 at $(1 + x, y, 1 + z)$, which lies in the adjacent sheets in the $-a$ direction, while atoms C15 and C23 at (x, y, z) both act as donors to atom O2 at $(1 + x, 1 + y, z)$. These paired C—H···O hydrogen bonds, combined with the O—H···N and N—H···O hydrogen bonds in the [211] chains, generate a second type of sheet, parallel to $(\bar{1}11)$ and containing four types of ring motif, $R_4^4(22)$, $R_4^4(16)$ and two types of $R_2^2(7)$ ring (Fig. 6). In these $(\bar{1}11)$ sheets, the adjacent [211] chains are components of different $(10\bar{2})$ sheets, and hence the C—H···O hydrogen bonds serve to link each $(10\bar{2})$ sheet to its two immediate neighbours.

Within the bipyridyl unit, the dihedral angle between the ring planes is 7.4(2)°. Each bipyridyl forms weak $\pi\cdots\pi$ stacking interactions with bipyridyl units in the two adjacent $(10\bar{2})$ sheets. Ring 1 (containing atom N11) of the bipyridyl at (x, y, z) forms a $\pi\cdots\pi$ interaction with ring 2 (containing atom N21) in the bipyridyl at $(x - 1, y, z)$, while ring 2 at (x, y, z) forms an identical interaction with ring 1 at $(1 + x, y, z)$.

3.2.2. 4,4′-Bipyridyl–(*S*)-malic acid (1/1) [*C*2 polymorph, (3)] and 4,4′-bipyridyl–*rac*-malic acid (1/1) [$P2_1/c$, (4)]. In the monoclinic polymorph (3), derived from (*S*)-malic acid, the two carboxylate groups of the (*S*)-malic acid unit form two hydrogen bonds with N atoms in two adjacent bipyridyl units, so forming chains of alternating malic and bipyridyl units. The hydroxyl group acts as a hydrogen-bond donor in O—H···O hydrogen bonds which link these chains into sheets, and

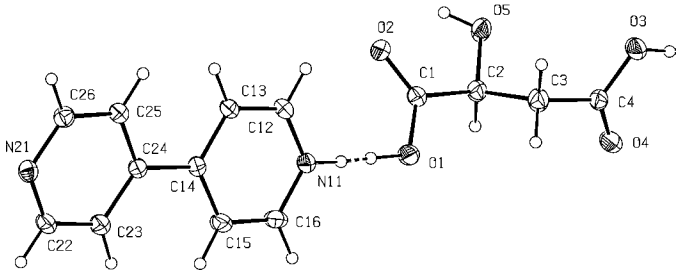

Figure 12
The molecular components of (4), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% probability level. The H atom between atoms O1 and N11 is disordered over two sites with equal occupancy.

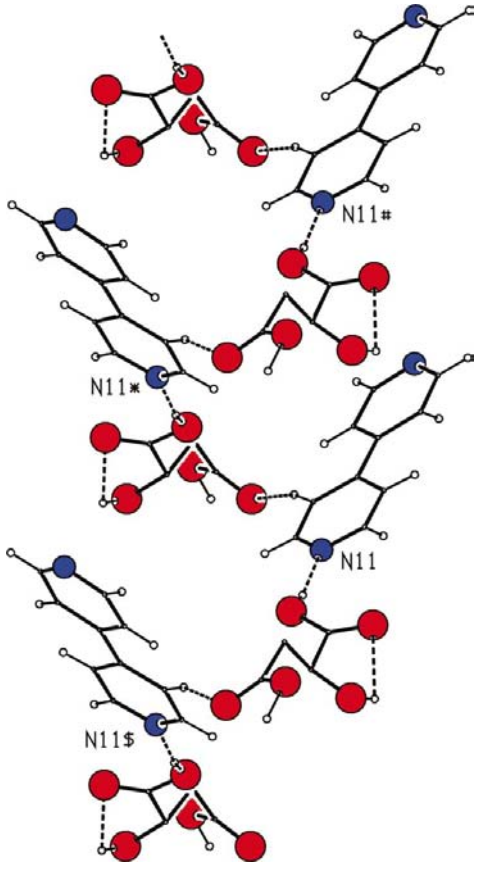

Figure 11
Part of the crystal structure of (3), showing the $C_2^2(11)$ chain motif formed by the soft hydrogen bonds which link the (100) sheets. For the sake of clarity, H atoms bonded to C atoms in the anion have been omitted. Likewise, the unit-cell box has been omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions $(-x, y - 1, 1 - z)$, $(x, y - 2, z)$ and $(-x, 1 + y, 1 - z)$, respectively.

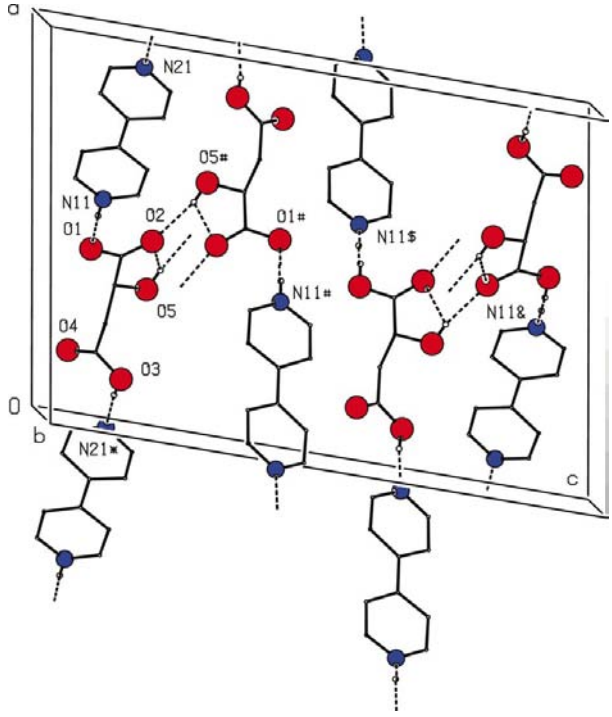

Figure 13
Part of the crystal structure of (4), showing the formation of the [120] and $[\bar{1}20]$ chains. For the sake of clarity, H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(x - 1, y - 2, z)$, $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(1 - x, 1 - y, 1 - z)$, respectively.

adjacent sheets are linked together by C—H···O hydrogen bonds.

Within the asymmetric unit (Fig. 7), there is a fully ordered O—H···N hydrogen bond between atoms O1 and N11. In the other hydrogen bond involving the bipyridyl unit, the H atom between atom O3 at (x, y, z) and atom N21 at (x, $2 + y$, $z - 1$) is disordered over two sites. These are located adjacent to O and N, respectively, at normal bonded distances and they have equal occupancy, so that there are equal numbers of O—H···N and N—H···O hydrogen bonds at sites of this type. It is entirely possible that the H atom in these hydrogen bonds is, in fact, mobile between alternative locations. The net effect of the carboxyl/N hydrogen bonds is to generate a $C_2^2(16)$ chain running parallel to the [02$\bar{1}$] direction (Fig. 8) and lying entirely within the domain $0 < x < \frac{1}{4}$. Four of these chains run through each unit cell. The chain within the domain $\frac{1}{2} < x < \frac{3}{4}$ is related to the reference chain by the *C*-centring and is also parallel to [02$\bar{1}$]. The chains in the domains $\frac{1}{4} < x < \frac{1}{2}$ and $\frac{3}{4} < x < 1$ are generated from the [02$\bar{1}$] chains by the action of the 2_1 screw axes, and thus they run parallel to [021]. Along the [100] direction, therefore, there are alternating domains of [02$\bar{1}$] and [021] chains. The chains in adjacent domains which are related by the 2_1 screw axes are linked by O—H···O hydrogen bonds. The hydroxyl atom O5 at (x, y, z), which lies in an [02$\bar{1}$] chain, acts as a hydrogen-bond donor to carboxyl atom O2 at ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $1 - z$), which is a component of an [021] chain. Atom O5 at ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $1 - z$) in turn acts as a donor to atom O2 at (x, $1 + y$, z), a component of the adjacent [02$\bar{1}$] chain. Propagation of this interaction links all of the chains in the domain $0 < x < \frac{1}{2}$ into a sheet parallel to (100) and centred at $x = \frac{1}{4}$. All the chains in the domain $\frac{1}{2} < x < 1$ are similarly linked into a second (100) sheet centred at $x = \frac{3}{4}$ (Figs. 8 and 9).

There are a number of C—H···O hydrogen bonds, in all of which the donors lie in the bipyridyl units. There are two such interactions, both nearly linear and with C···O < 3.50 Å and H···O < 2.50 Å, which serve to link adjacent (100) sheets. Atom C16 in the bipyridyl unit at (x, y, z) is a component of

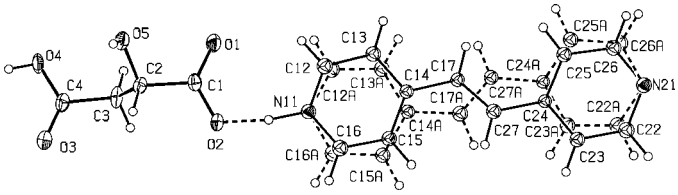

Figure 14
The molecular components of (5) showing the atom-labelling scheme. The minor component of the disordered diamine is depicted with dotted lines. Displacement ellipsoids (isotropic for both components of the diamine) are shown at the 30% probability level.

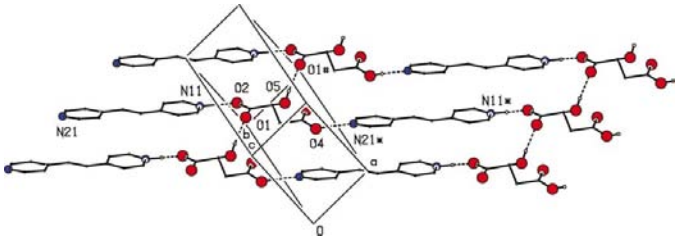

Figure 15
Part of the crystal structure of (5) showing the formation of an (01$\bar{1}$) sheet built from $R_6^6(44)$ rings. For the sake of clarity, only the major component of the diamine is shown and H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($3 + x$, $y - 1$, $z - 1$) and ($1 + x$, y, z), respectively.

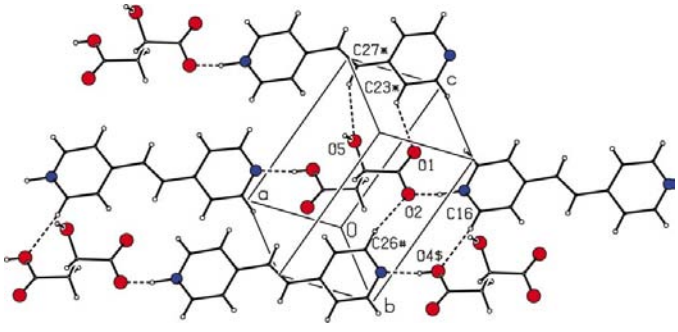

Figure 16
Part of the crystal structure of (5) showing the linking of the (01$\bar{1}$) sheets by C—H···O hydrogen bonds For the sake of clarity, only the major component of the diamine is shown. The atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions ($2 + x$, $y - 1$, z), ($2 + x$, y, $z - 1$) and ($x - 1$, $1 + y$, z), respectively.

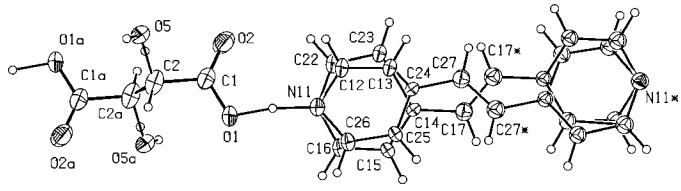

Figure 17
The molecular components of (6) showing the atom-labelling scheme. The atoms marked with an asterisk (*) in the diamine or with '*a*' in the acid are at the symmetry positions ($-2 - x$, $2 - y$, $2 - z$) and ($1 - x$, $1 - y$, $1 - z$), respectively. The acid component is disordered across a centre of inversion, so that if atom O5 is present [(*S*)-malic acid], then O5*a* is absent, while if atom O5*a* is present [(*R*)-malic acid], O5 is absent. Displacement ellipsoids are shown at the 30% probability level.

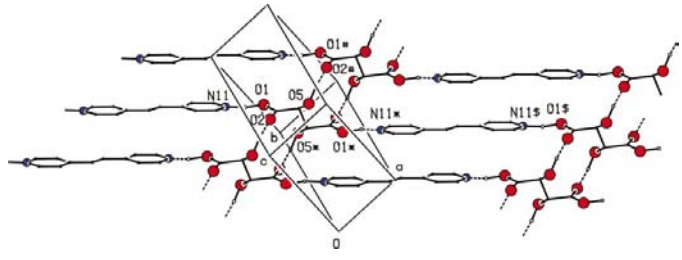

Figure 18
Part of the crystal structure of (6) showing the linking of [$\bar{3}$11] chains into an (01$\bar{1}$) sheet. All atom sites of type O5 have 0.5 occupancy. Hence, this figure shows the average arrangement of the O—H···O hydrogen bonds, all having 0.5 occupancy (see text). For the sake of clarity, H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions ($1 - x$, $1 - y$, $1 - z$), ($1 + x$, y, z) and ($3 + x$, $y - 1$, $z - 1$), respectively.

the (100) sheet centred at $x = \frac{1}{4}$. This atom acts as a hydrogen-bond donor to atom O1 at $(-x, y, 1 - z)$, which lies in the (100) sheet centred at $x = -\frac{1}{4}$. Propagation of this interaction leads to the formation of centrosymmetric $R_4^4(10)$ rings (Fig. 10). Similarly, atom C15 at (x, y, z) acts as a hydrogen-bond donor to atom O4 at $(-x, y - 1, 1 - z)$, also a component of the (100) sheet centred at $x = -\frac{1}{4}$, while atom C15 at $(-x, y - 1, 1 - z)$ in turn acts as a donor to atom O4 at $(x, y - 2, z)$, so generating a $C_2^2(11)$ chain parallel to [010] (Fig. 11), which also links the two (100) sheets centred at $x = \frac{1}{4}$ and $x = -\frac{1}{4}$.

On the opposite face of the sheet centred at $x = \frac{1}{4}$, atoms C15 and C16 at $(\frac{1}{2} - x, \frac{1}{2} + y, 1 - z)$ act as donors to atoms O4 and O1 at $(\frac{1}{2} + x, -\frac{1}{2} - y, z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, z)$, respectively, which both lie in the (100) sheet centred at $x = \frac{3}{4}$. Thus, each (100) sheet, formed by hard hydrogen bonds of types O—H···O, O—H···N and N—H···O, is linked to two adjacent sheets by soft hydrogen bonds of the type C—H···O, so forming a continuous three-dimensional supramolecular structure.

The structure of (4) derived from racemic malic acid shows a number of features in common with that of (3), as well as a number of differences. The selected asymmetric unit of (4) (Fig. 12) comprises one bipyridyl unit and one (*S*)-malic acid unit. As in (3), the carboxyl groups of the acid unit and the N atoms of the bipyridyl unit participate in mutual hydrogen-bond formation, again generating $C_2^2(16)$ chains. However, in (4) it is the hydrogen bond within the asymmetric unit, involving atoms O1 and N11, where the H atom is disordered over two sites with equal occupancy. In the other hydrogen bond within the $C_2^2(16)$ chain, the H atom is fully ordered, on atom O3, and atom O3 at (x, y, z) acts as a hydrogen-bond donor to atom N21 at $(x - 1, y - 2, z)$, so generating a chain running parallel to the [120] direction (Fig. 13). There are [120] chains in the domains $0 < z < \frac{1}{4}$ and $\frac{1}{2} < z < \frac{3}{4}$, and [$\bar{1}$20] chains in the domains $\frac{1}{4} < z < \frac{1}{2}$ and $\frac{3}{4} < z < 1$. As in (3), the chains in adjacent domains related by the 2_1 screw axes are linked into sheets. Hydroxyl atom O5 at (x, y, z), which lies in

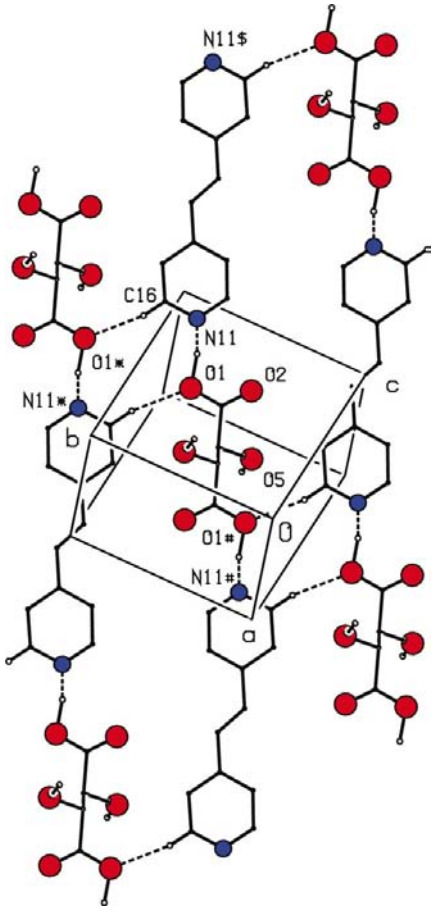

Figure 19
Part of the crystal structure of (6) showing the linking of [$\bar{3}$11] chains into a (1$\bar{2}\bar{2}$) sheet by means of C—H···O hydrogen bonds. All atom sites of type O5 have 0.5 occupancy. Hence, this figure shows the average arrangement of the O—H···O hydrogen bonds, all having 0.5 occupancy (see text). For the sake of clarity, H atoms bonded to C atoms but not involved in the hydrogen-bonding motifs shown have been omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions $(-x, 2 - y, 1 - z)$, $(1 - x, 1 - y, 1 - z)$ and $(-2 - x, 2 - y, 2 - z)$, respectively.

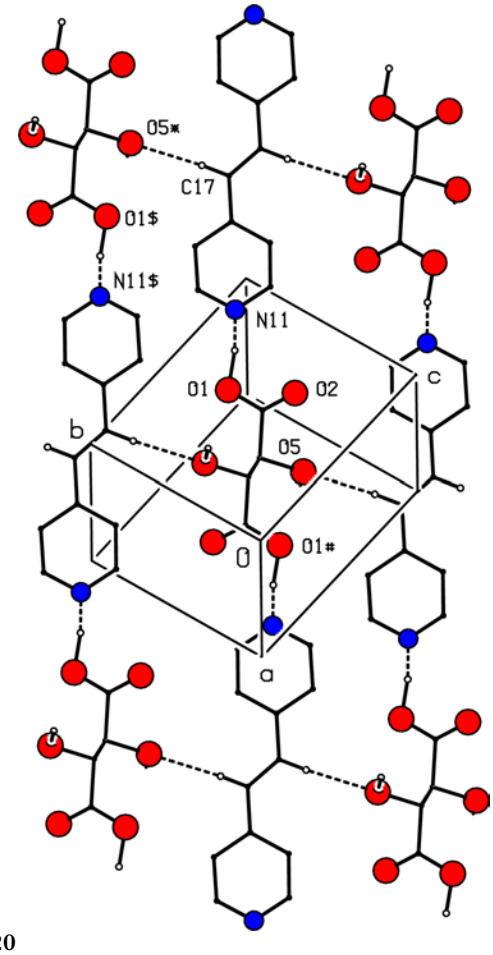

Figure 20
Part of the crystal structure of (6) showing the linking of [$\bar{3}$11] chains into a (121) sheet by means of C—H···O hydrogen bonds. All atom sites of type O5 have 0.5 occupancy. Hence, this figure shows the average arrangement of the O—H···O hydrogen bonds, all having 0.5 occupancy (see text). For the sake of clarity, H atoms bonded to C atoms but not involved in the hydrogen-bonding motifs shown have been omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions $(x - 2, 1 + y, z)$, $(1 - x, 1 - y, 1 - z)$ and $(-1 - x, 2 - y, 1 - z)$, respectively.

a [120] chain, acts as a hydrogen-bond donor to carboxyl atom O2 at $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$, which lies in a $[\bar{1}20]$ chain, while atom O5 at $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$, in turn, acts as a donor to atom O2 at $(x, y-1, z)$, a component of the adjacent [120] chain.

In this manner, a sheet parallel to (001) is formed, lying across the plane $z = \frac{1}{4}$. A second (001) sheet lies across the plane $z = \frac{3}{4}$. In (3) the two (100) sheets in the unit cell are related by the *C*-centring operation, and both contain the same enantiomer of malic acid. In (4) the two (001) sheets are related by centres of inversion; that across $z = \frac{1}{4}$ contains only the (*S*)-enantiomer of malic acid, while that across $z = \frac{3}{4}$ contains only the (*R*)-enantiomer.

There are two nearly linear C—H···O hydrogen bonds in (4), with C···O < 3.50 and H···O < 2.50 Å (Table 2), which serve to link each (001) sheet to its two neighbours, [*cf.* (3)]. Atoms C16 and C23 in the bipyridyl at (x, y, z) lie in the sheet across $z = \frac{1}{4}$, and they act as hydrogen-bond donors to atoms O1 and O4, respectively, in the malic acid unit at $(1-x, 1-y, -z)$, which is a component of the sheet across $z = -\frac{1}{4}$. On the opposite face of the $z = \frac{1}{4}$ sheet, atoms C16 and C23 at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ act as hydrogen-bond donors to atoms O1 and O4 at $(x, \frac{3}{2}-y, \frac{1}{2}+z)$, which lie in the (001) sheet across $z = \frac{3}{4}$.

3.2.3. General comparison of (2)–(4). Each of the adducts (2)–(4) has 1:1 stoichiometry and each is a salt in which both of the carboxylate H atoms are partially transferred to the two N atoms of the diamine. In each the basic structural motifs are chains of alternating bipyridyl and malate units, always generated by translation, and the coupling of these chains by means of O—H···O hydrogen bonds involving the malate hydroxyl groups as donors. Each chain in each structure exhibits both direction, or polarity, and chirality. Both properties arise from the disposition of the hydroxyl group in the malate units. The position of this substituent on the carbon chain defines the polarity of the chain, and the configuration at the stereogenic centre C2 defines the chirality. It is the different arrangements of the translational chains within the structure, as defined by their polarity and chirality (Figs. 5, 8 and 13), which distinguishes the supramolecular structures of (2)–(4).

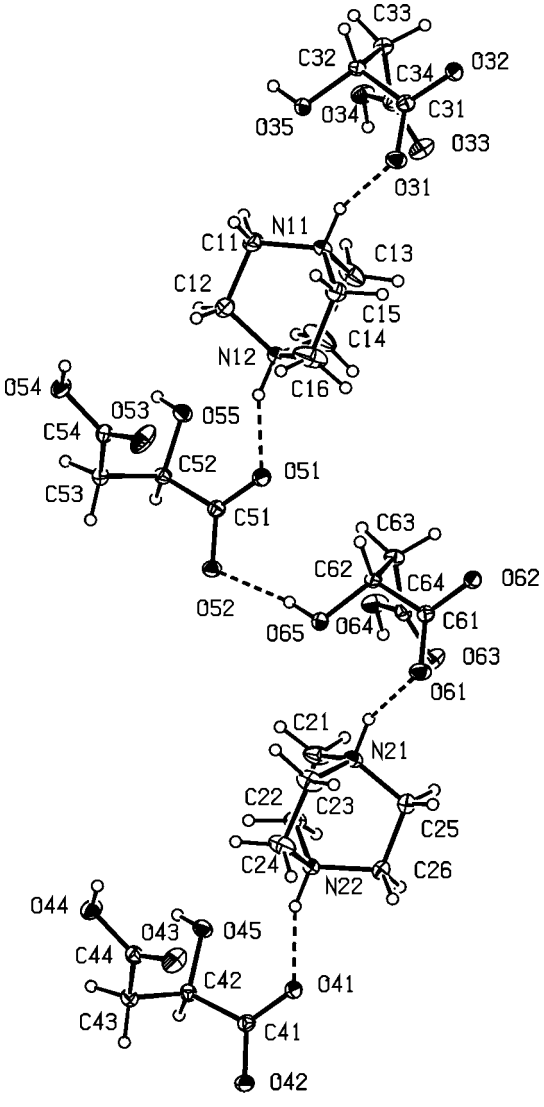

Figure 21
The six molecular components of (7), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% probability level.

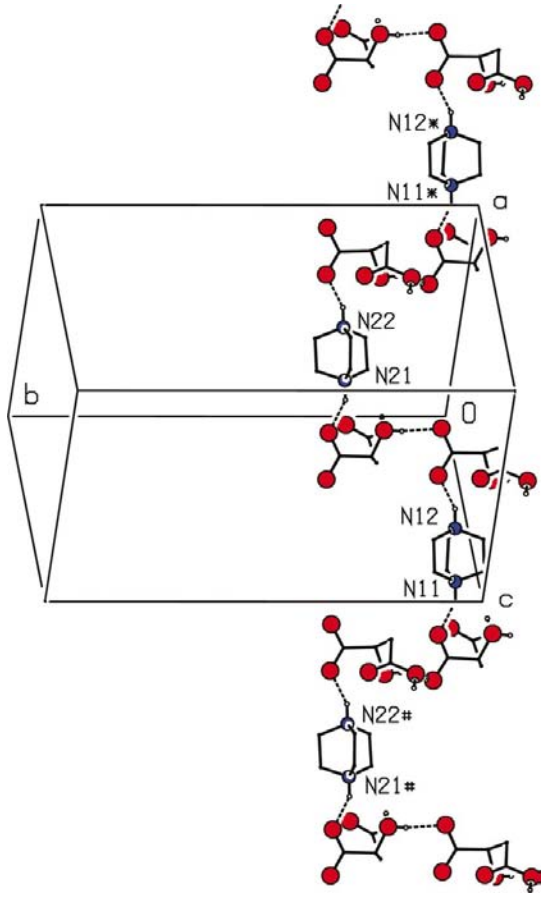

Figure 22
Part of the crystal structure of (7), showing the formation of a $C_6^6(28)$ chain parallel to $[10\bar{1}]$. For the sake of clarity, H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1+x, y, z-1)$ and $(x-1, y, 1+z)$, respectively.

3.2.4. Salts of 1,2-bis(4′-pyridyl)ethene with malic acids, (5) and (6). In the 1:1 adduct, compound (5), formed between 1,2-bis(4′-pyridyl)ethene and (*S*)-malic acid, there is complete transfer of the H atom from one of the carboxyl groups to atom N11 of the diamine, giving a salt, $(C_{12}H_{10}N_2)H^+\cdot C_4H_5O_5^-$ (Fig. 14). The diamine is itself disordered over two sets of sites, as observed in the adduct of this diamine with 4,4′-sulfonyldiphenol (Ferguson *et al.*, 1999). The supramolecular structure of (5) is dominated by hard hydrogen bonds of types O—H···N and O—H···O (Table 2), which link the ionic components into sheets, which are themselves linked by C—H···O hydrogen bonds.

Within the asymmetric unit (Fig. 14), the pyridyl atom N1 acts as a hydrogen-bond donor to the carboxylate atom O2. In addition,the carboxyl atom O4 at (x, y, z) acts as a donor to the pyridyl atom N21 at $(3 + x, y - 1, z - 1)$, so generating, by translation, a $C_2^2(18)$ chain running parallel to the $[\bar{3}11]$ direction (Fig. 15). There is just one of these chains running through each unit cell, but the parallel chains are linked into sheets parallel to $(01\bar{1})$ by O—H···O hydrogen bonds. The hydroxyl atom O5 at (x, y, z) acts as a donor to the carboxylate atom O1 at $(1 + x, y, z)$, so generating, by translation, a $C(5)$ chain parallel to [100]. The combination of the $[\bar{3}11]$ and [100] chains generates the $(01\bar{1})$ sheet built from a single type of $R_6^6(44)$ ring (Fig. 15).

Adjacent sheets are linked by the cooperative effect of four C—H···O hydrogen bonds. Atom C16 at (x, y, z) acts as a hydrogen-bond donor to atom O4 at $(x - 1, 1 + y, z)$, while atom C26 at $(2 + x, y, z - 1)$, in the same $[\bar{3}11]$ chain as atom O4 at $(x - 1, 1 + y, z)$, acts as a donor to atom O2 at (x, y, z) in the original chain. Similarly, atoms C23 and C27 at $(2 + x, y - 1, z)$ act as donors to atoms O1 and O5, respectively, at (x, y, z) (Fig. 16). Propagation of these C—H···O hydrogen bonds links all of the $(01\bar{1})$ sheets into a continuous three-dimensional framework.

The 1:1 adduct (6), formed between 1,2-bis(4′-pyridyl)-ethene and racemic malic acid, crystallizes in space group $P\bar{1}$, with $Z' = 0.5$. The acid component (Fig. 17) is disordered across a centre of inversion, chosen for convenience as that at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, such that half of these sites accommodate molecules of (*S*)-configuration and half accommodate molecules of (*R*)-configuration. If a molecule of (*S*)-malic acid occupies any particular acid site, then atom O5 is present and O5*a* is absent (Fig. 17); occupation by (*R*)-malic acid means that atom O5*a* is present and O5 is absent. The diamine also lies across a centre of inversion, at (−1,1,1), and it adopts two orientations, as in (5), but in this case having equal occupancies. Also as in (5), the N atoms in the two orientations were constrained to have identical coordinates. The occupancy of a common site by disordered (*R*) and (*S*) enantiomers necessarily raises the question (Marsh, 1999) *P*1 or $P\bar{1}$? However, all attempts at structure solution in *P*1 failed and, moreover, the unit-cell dimensions are consistent with the presence of only one molecule of each component in the cell. A *P*1 cell with $Z' = 1$ could thus not accommodate the racemic acid. A rather similar problem arose in the structure of racemic [*cis*-dichlorobis(pentane-2,4-dionato)titanium(IV)], where a common molecular site in the space group $P\bar{1}$ is occupied by equal proportions of the Λ and Δ enantiomers, and where again the alternative space group *P*1 was decisively rejected (Ferguson & Glidewell, 2001).

Within the asymmetric unit of (6) (Fig. 17), atom H1 is almost mid-way between atoms O1 and N11, so that the H-

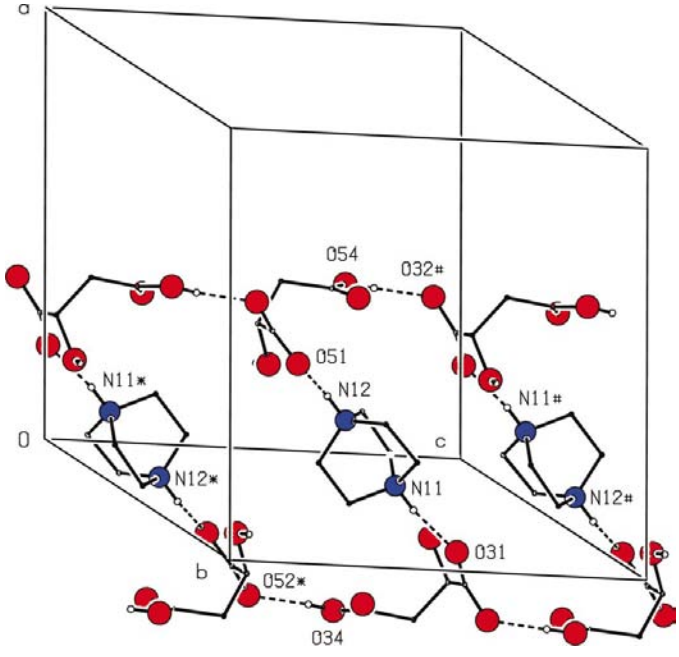

Figure 23
Part of the crystal structure of (7), showing the formation of a molecular ladder along [001] generated by inversion. For the sake of clarity, H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-x, -y, 1 - z)$ and $(-x, -y, 2 - z)$, respectively.

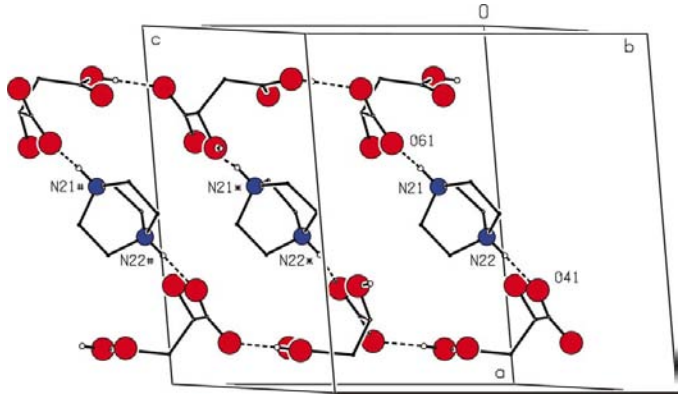

Figure 24
Part of the crystal structure of (7), showing the formation of a molecular ladder along [001] generated by the glide plane at $y = \frac{1}{4}$. For the sake of clarity, H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(x, y, 1 + z)$, respectively.

atom transfer is best regarded as partial. Since both components lie across centres of inversion, propagation of the single O···H···N hydrogen bond generates, by inversion, a $C_2^2(18)$ chain running parallel to the [$\bar{3}$11] direction (Fig. 18). These chains are linked by O—H···O hydrogen bonds but, because of the (*R*)/(*S*) disorder at the acid sites, the number of O—H···O hydrogen bonds linking a pair of adjacent malic acid molecules may in fact be two, one or none, depending upon the local arrangement of the enantiomers. If it is assumed, without loss of generality, that the acid at ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) (denoted as molecule *A*) has (*S*)-configuration, then its two immediate neighbours, at ($\frac{3}{2},\frac{1}{2},\frac{1}{2}$) (molecule *B*) and at ($-\frac{1}{2},\frac{1}{2},\frac{1}{2}$) (molecule *C*), can each have either (*R*)- or (*S*)-configuration, independently. If molecules *B* and *C* both have (*S*)-configuration, then these three molecules are linked by a fragment of a *C*(5) chain running parallel to [100] (Fig. 18). If molecules *B* and *C* have (*R*)- and (*S*)-configurations, respectively, then molecules *A* and *B* are linked by an $R_2^2(12)$ motif centred at ($1,\frac{1}{2},\frac{1}{2}$), while molecules *A* and *C* are linked as before. When molecules *B* and *C* have (*S*)- and (*R*)-configurations, respectively, then molecules *A* are *B* are linked by a *C*(5) chain fragment, while molecules *A* and *C* are not linked directly by any O—H···O hydrogen bonds. Finally, if molecules *B* and *C* both have (*R*)-configuration, then molecules *A* and *B* are again linked in an $R_2^2(12)$ motif, while molecules *A* and C are again not linked directly. A similar, but reversed, set of possibilities arises if molecule *A* is assumed to be of (*R*)-configuration. These possible arrangements of the O—H···O hydrogen bonds are distributed in an uncorrelated fashion throughout the structure and their effect is to link the [$\bar{3}$11] chains into an (01$\bar{1}$) sheet (Fig. 18), but the ring structure within this sheet itself depends upon the detailed local arrangement of the O—H···O hydrogen bonds.

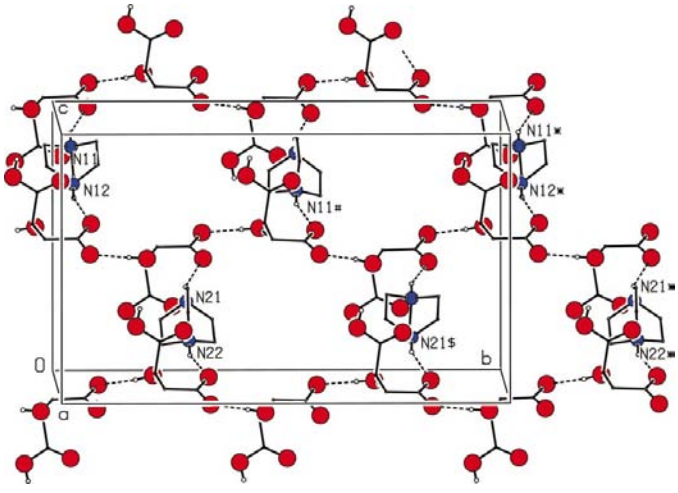

Figure 25
Part of the crystal structure of (7), showing the formation of a (100) sheet by combination of $C_4^4(19)$ spiral chains parallel along (0, *y*, $\frac{3}{4}$) and ($\frac{1}{2}$, *y*, $\frac{1}{4}$). For the sake of clarity, H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions ($x, 1+y, z$), ($-x, \frac{1}{2}+y, \frac{3}{2}-z$) and ($1-x, \frac{1}{2}+y, \frac{1}{2}-z$), respectively

There are two C—H···O hydrogen bonds in (6) which are structurally significant (Table 2), and these combine to link the (01$\bar{1}$) sheets into a three-dimensional framework. Atom C16 at (*x*, *y*, *z*) acts as a hydrogen-bond donor to atom O1 at ($-x$, $2-y$, $1-z$), and propagation of this hydrogen bond by the centres of inversion links the [$\bar{3}$11] chains into a sheet parallel to (1$\bar{2}$2) (Fig. 19). Atom C17 at (*x*, *y*, *z*) similarly acts as a donor to the hydroxyl atom O5 at ($x-2, 1+y, z$). Subject to the 0.5 occupancy of the O5 site, propagation of this hydrogen bond links the [$\bar{3}$11] chains into a sheet parallel to (121) (Fig. 20). The combination of the (01$\bar{1}$), (1$\bar{2}$2) and (121) sheets generates a three-dimensional framework.

3.3. Hard hydrogen bonds generate three-dimensional arrays

3.3.1. 1,4-Diazabicyclo[2.2.2]octane–racemic malic acid (1/2) (7). Compound (7) is a 1:2 adduct, DABCO·2(malic acid), which crystallizes in space group $P2_1/c$ with $Z' = 2$. Hence, there are six independent molecular components in the asymmetric unit, and there is complete transfer of one H atom by each acid unit, from the carboxyl group adjacent to the hydroxyl to the DABCO unit. The compound is thus a salt, $(C_6H_{12}N_2)H_2^{2+}\cdot 2C_4H_5O_5^-$, in which the component ions are linked by an extensive array of N—H···O and O—H···O hydrogen bonds into a three-dimensional framework. The selection of the asymmetric unit allows a wide choice. Although the space group accommodates equal numbers of (*R*)- and (*S*)-malic acid units, the asymmetric unit selected, which permits a linear arrangement of the six components (Fig. 21), contains four acid units all having the (*R*)-configuration.

As well as the four N atoms, all four hydroxyl groups, containing atoms O*n*5 (*n* = 3–6), and all four carboxyl groups, containing atoms O*n*4 (*n* = 3–6), act as hydrogen-bond donors. Each of the carboxylate O atoms O*n*1 (*n* = 3–6) acts as a single acceptor from N, while the corresponding atoms O*n*2 (*n* = 3–6) all act as double acceptors. Each atom O*n*2 accepts one hydrogen bond from a hydroxyl donor and one from a carboxyl donor. However, in the neutral carboxyl groups, neither the O*n*3 nor the O*n*4 atoms act as acceptors in O—H···O or N—H···O hydrogen bonds, nor do the hydroxyl O*n*5 atoms. Of the eight O—H···O hydrogen bonds, only two, those with atoms O44 and O64 as the hydrogen-bond donors, involve the same type of molecular unit as both donor and acceptor.

Although the coordinates of the majority of the atoms in the odd-numbered molecular units, containing atoms N11, C31 and C51 (Fig. 21), can be approximately related to those in the corresponding even-numbered units (containing atoms N21, C41 and C61) by the translation ($\frac{1}{2}+x, \frac{1}{4}+y, z-\frac{1}{2}$), the orientations of the two DABCO skeletons indicate that no such relationship can apply to the C atoms in the cations, so precluding any possibility of additional symmetry.

Within the asymmetric unit, there are four N—H···O hydrogen bonds all linking a cation to an anionic carboxylate O atom. All four of these hydrogen bonds are short for their type, with N···O < 2.65 Å and H···O < 1.80 Å, since, in each

example, the hydrogen-bond donor and acceptor are both charged (Aakeröy & Seddon, 1993; Gilli *et al.*, 1994). There is a single O—H···O hydrogen bond within the asymmetric unit linking atoms O65 and O52 and, in addition, atom O45 at (x, y, z) acts as a hydrogen-bond donor to atom O32 at ($1 + x$, y, $z - 1$). These six hydrogen bonds thus generate, by translation, a $C_6^6(28)$ chain running parallel to the [10$\bar{1}$] direction, in which the H atoms in the six hydrogen bonds are all fully ordered (Fig. 22). There are four such chains passing through each unit cell and the formation of the three-dimensional framework is most readily analysed in terms of the motifs linking these chains. Two types of [001] motif combine to generate (010) sheets, and two types of [010] motif combine to generate (100) sheets. The combination of (100) and (010) sheets generates the three-dimensional framework. Similarly, the combination of [10$\bar{1}$] chains with the [010] or [001] motifs generates (101) and (010) sheets, respectively. Thus, sub-structures in both one and two dimensions can be identified within the overall framework.

The hydroxyl atom O34 at (x, y, z) acts as a hydrogen-bond donor to the carboxylate atom O52 at ($-x$, $-y$, $1 - z$), thus generating an $R_6^6(32)$ ring centred at (0,0,$\frac{1}{2}$) which links an antiparallel pair of chains (Fig. 23). One chain in each pair contains only (*R*)-malate anions, the other only (*S*)-malate anions. In similar fashion, the hydroxyl atom O54 at (x, y, z) acts as a hydrogen-bond donor to the carboxylate atom O32 at ($-x$, $-y$, $2 - z$), generating a second $R_6^6(32)$ motif, this time centred at (0,0,1). The combination of these two motifs produces a molecular ladder along [001], generated by inversion. There is a second molecular ladder parallel to [001], but generated by the glide plane at $y = \frac{1}{4}$. The hydroxyl atom O64 at (x, y, z) acts as a hydrogen-bond donor to the carboxylate atom O62 at (x, $\frac{1}{2} - y$, $z - \frac{1}{2}$), while atom O64 at (x, $\frac{1}{2} - y$, $z - \frac{1}{2}$), in turn, acts as a donor to atom O62 at (x, y, $z - 1$) (Fig. 24). Similarly, atom O44 at (x, y, z) acts as a donor to atom O42 at (x, $\frac{1}{2} - y$, $\frac{1}{2} + z$), so generating an antiparallel chain. The combination of these two chains and the cation linking them generates the second [001] ladder, and the O65—H65···O52 hydrogen bond links the two types of ladder into a continuous (010) sheet.

Two further one-dimensional motifs generate the (100) sheets. The hydroxyl atom O35 at (x, y, z) acts as a hydrogen-bond donor to the carboxylate atom O62 at ($-x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$), while atom O35 at ($-x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$), in turn, acts as a donor to atom O62 at (x, $y - 1$, z). In this manner, a $C_4^4(19)$ spiral is generated around the 2_1 screw axis along (0, y, $\frac{3}{4}$), within which the repeat pattern consists of three malate units and one diamine unit (Fig. 25). Similarly, atom O55 at (x, y, z) acts as a hydrogen-bond donor to atom O42 at ($1 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$), producing a second $C_4^4(19)$ spiral around the 2_1 screw axis along ($\frac{1}{2}$, y, $\frac{1}{4}$). These two motifs generated by screw axes parallel to the [010] direction combine to form the (100) sheet.

There are a number of C—H···O hydrogen bonds having H···O < 2.50 Å (Table 2); all the C—H donors are in the cations and all are adjacent to cationic N atoms. Since the hard hydrogen bonds generate a three-dimensional framework, the soft hydrogen bonds simply serve to reinforce this.

3.4. Chirality, pseudosymmetry and polymorphism

For the structures formed by the bipyridyl species, in particular (3)–(6), it is striking how similar, in general terms, are the architectures of the chiral and racemic pairs, (3)/(4) and (5)/(6). In the case of (3) and (4), where the space groups are $C2$ and $P2_1/c$, respectively, the overall structure can be envisaged as arising from a pair of chains having the same chirality but opposite polarity and related to each other by the 2_1 screw axis. From this common partial structure, the complete structures of (3) and (4) can be simply derived by the actions of the *C*-centring operation in (3) and of the centres of inversion in (4). Compounds (5) and (6) exhibit very similar supramolecular architectures, in space groups $P1$ and $P\bar{1}$, respectively, with 88% of the non-H atoms in the anions in (5) conforming to the centrosymmetric space group. The main non-fitting atom is the hydroxyl O atom. Likewise, in (1), where the close mimicry of $P\bar{1}$ has already been noted (§3.1), and (2), 92% and 85%, respectively, of the non-H atoms in $P1$ conform to $P\bar{1}$. The two DABCO adducts (7) and (8), while exhibiting different stoichiometries and thus different supramolecular structures, again conform to the general expectation that the different forms of malic acid will lead to different space groups. Here, the salts crystallize in $P2_1/c$ and $P2_1$, respectively.

The two polymorphs, (2) and (3), crystallized concurrently from a single solution in methanol; although the ratio of products obtained was not quantified, the yields were rather similar. We have observed a similar cocrystallization of two polymorphs, one triclinic, $P\bar{1}$, and the other orthorhombic, *Pbca*, from an ethanol solution of 2-iodo-4-nitroaniline (McWilliam *et al.*, 2001). It may be deduced that since the free energies of formation of the two crystalline forms in each case are unlikely to be identical, the kinetics of crystal growth may also be important. Rather little is currently known about polymorph formation of solvent-free cocrystals, although for single-component systems it is possible, in favourable cases, for very large numbers of solvates (pseudopolymorphs) to be formed (Bingham *et al.*, 2001).

4. Concluding comments

The supramolecular structures reported and analysed in this paper indicate clearly that where chiral and racemic forms of malic acid, an exemplar of simple chiral acids, form adducts of common stoichiometry with a given diamine, then the overall supramolecular structures of the two products are remarkably similar, despite the different space groups exhibited. Indeed, the structures involving the chiral acid closely mimic centrosymmetry in a number of cases. Against this useful generalization, it is noted that even the product stoichiometries observed here are, in a number of cases, neither predictable nor amenable to simple rationalization, despite the chemical simplicity of the molecular building blocks employed.

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